

Formation of TiO₂ composites on activated carbon modified by nitric acid and their photocatalytic activity

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We have studied a method for the preparation of carbon/TiO₂ composites involving the penetration of titanium n-butoxide (TNB) solution into activated carbon. The study has focused on the characterization of the TiO₂ obtained in the porous carbon and how increased surface functional groups were created by the acid treatment. The conversion of TNB to TiO₂ during the heat treatment must be important for the preparation of carbon/TiO₂ composites. From the surface textural properties, both the BET surface area and the total pore volume decreased with the distribution of TiO₂ on the activated carbon surfaces after the acid treatment. According to the results of SEM micrographs, titanium complex particles were regularly distributed on the carbon. Also some large clusters were found when the amount of acid treatment was increased. The changes in XRD patterns show typical anatase type on carbon/TiO₂ composites prepared with activated carbon modified by nitric acid. The EDX results of carbon/TiO₂ composites show the presence of C, O and S with strong Ti peaks. Observation of the absorption bands for the FT-IR spectra shows that the changes for the carbon/TiO₂ composite prepared with activated carbon modified by nitric acid are mainly due to the formation of functional groups. Finally, the excellent photocatalytic activity of carbon/TiO₂ composites between relative concentration (c/c_0) of MB and UV irradiation time could be attributed to both effects between photocatalysis of the formation of titania complexes and the adsorptivity of the activated carbon.

Key words: Carbon, TNB, BET, SEM, XRD, EDX, FT-IR, Photocatalytic activity.

Introduction

The decomposition of environmental pollutants using TiO₂ photocatalysts has been one of the most promising methods for dealing with this problem [1, 2]. Also, activated carbons and their fibers have been extensively used as adsorbents in industrial technologies related to environmental pollution control due to their well-developed pore structure and excellent adsorption capacity [3-5]. Titanium dioxide has also been widely studied as a promising material for an environmental protection approach for the past few decades because of its excellent photocatalytic activity. A number of studies have shown their unique performance in the photodegradation of most organic toxic compounds in wastewater [6, 7]. As TiO₂ and related compounds show interesting catalytic or dielectric properties, they have been widely studied in terms of the preparation of materials with large surface areas. For some practical applications, the photocatalyst TiO₂ particles were either mounted on porous adsorbents such as activated carbons and zeolites, or fixed on substrates using a binder. In the former case, the pollutant molecules could be adsorbed onto the adsorbents, but they were not readily

decomposed by the TiO₂ photocatalysts mainly because of the slow diffusion speed of the pollutants on the adsorbent surfaces of the TiO₂ particles. According to former studies for carbon sources, the carbonization of an unlinked resorcinol resin with titanium tetrabutoxide [8], the immersion of activated carbon in a TiO₂ sol [9], and the mechanical grinding of activated carbon with TiO₂ [10] have been reported for the preparation of carbon/TiO₂ composites. A composite product of activated carbon and TiO₂ photocatalyst may offer the merits such as an adsorption effect on the porous structure and a light excitation source for the photocatalytic degradation of the pollutants. However, the penetration of TiO₂ in the pores is restricted with the above mentioned methods. We have studied a method for the preparation of carbon/TiO₂ composites involving the penetration of titanium n-butoxide (TNB) solution into activated carbon. This method is expected to have some advantages compared with liquid solvents for the coating process due to its high diffusivity, non-condensation and weak salvation properties. The concept is that TNB could penetrate into the micropore and mesopore structures of activated carbon and other porous materials and become adsorbed in pores as TNB molecules. The adsorbed TNB on the solid surface is then converted to TiO₂ through thermal decomposition and hydrolysis. The most common functional groups are carboxylic, carbonyls, phenols and lactones. Functional groups on the surface of microporous carbons are most likely

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subjected to a wide variety of inter- and intra-molecular interactions including inductive, mesomeric, tautomeric, steric and hydrogen bonding [11, 12]. These interactions may severely alter their Brønsted-acid-base characteristics in such a way that in most cases they may not resemble those of the parent chemical compounds. These functional groups may play role in the sorption and deposition of nonpolar molecules and metallic ions by creating obstacles for physical adsorption and preventing molecules from occupying the most energetically favorable positions on carbon surfaces [12-15]. Because of the increase of surface functional groups on the carbon surfaces by an acid treatment, the conversion of TNB to TiO₂ in pores or surfaces in activated carbons should be a complicated process.

In this study, we have focused on the characterization of the TiO₂ obtained in the porous carbon and how increased surface functional groups by acid treatment were created. The conversion of TNB to TiO₂ during the heat treatment must be important for the preparation of carbon/TiO₂ composites. Moreover, morphological studies of the converted TiO₂ should show how strongly affected by the porous structure of carbons, if the TiO₂ was properly formed in the restricted space within carbon. We have studied the chemical and morphological structure of carbon/TiO₂ composites by means of BET surface area, X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), FT-IR and UV/VIS spectroscopy.

Experimental

Materials

A porous and granular activated carbons used in this study was prepared from coconut shell. The coconut shell was pre-carbonized first at 773 K, and then activated by steam diluted with nitrogen in a cylindrical quartz tube at temperature of 1023 K for 30 minutes. These activated carbons were washed with deionized water and dried overnight in a vacuum dry oven at 683 K. The TiO₂ photocatalyst used was commercially available (Duk-San Pure Chemical Co., Korea), which was composed of a single phase of anatase with secondary particles of about 80-150 μm aggregated from the primary particles of about 30-50 μm. This anatase-type titanium dioxide powder had a relatively large BET surface area of about 125 m²/g. A molar concentration of from 0.05 to 0.5 M diluted nitric acid at boiling temperature was

used in the oxidation treatment to increase the formation of functional groups without damaging of the activated carbon surface. The oxidation was carried out at boiling temperature for 1 h. The oxidized activated carbons were washed and dried at 323 K for 24 h. We prepared activated carbon slurry solutions with pristine concentrations of 20 ml of titanium n-butoxide (TNB, C₁₆H₃₆O₄Ti, Acros Organics, USA) for the preparation of carbon/TiO₂ composites. For the preparation, 5 g of powdered activated carbon were mixed into 20 ml of TNB aqueous solution and stirred for 5 hours at 333 K. Then, the powder mixtures of TNB with activated carbon were heated at 973 K for 1 h. Before heat treatment, the solvent in the mixtures was vaporized at 343 K for 1 hour. The nomenclatures of the samples preparative were listed in Table 1.

Characterization

For physical parameter measurements, the BET specific surface areas were measured using a Quantachrome Autosorb Automated Gas System (Quantachrome Corporation, U.S.A) at 77 K. Scanning electron microscopy (SEM, JSM-5200 JOEL, Japan) was used to observe the surface state and structure of carbon/TiO₂ composites. For the elemental analysis in carbon/TiO₂ composites, energy dispersive X-ray analysis (EDX) was also used. X-ray diffraction patterns were taken using an X-ray generator (Shimatz XD-D1, Japan) with CuKα radiation. As one of the analyses of photocatalytic activity, a UV/VIS spectrophotometer (Genspec III (Hitachi), Japan) was used to characterize of the catalytic efficiency of carbon/TiO₂ photocatalysts. As one of the analyses of functional groups, FT-IR spectroscopy (FTS 3000MX, Biorad Co.) was used to characterize the titanium oxide loading effect of carbon/TiO₂ composites. The carbon/TiO₂ composites before and after nitric acid treatment were examined by the KBr method using the FT-IR spectroscopy. Discs for the method were prepared by first mixing 1 mg of powdered carbon/TiO₂ composite with 600 mg of KBr (for FTIR spectroscopy) in an agitate mortar, and then pressing the resulting mixture successively under a pressure of 450 kg/cm² for 3 minutes. The spectra of the samples were measured between 4000 and 500 cm⁻¹. Characterization of methylene blue (C₁₆H₁₈N₃S, MB) in water was determined by the following procedure. A carbon/TiO₂ composites powdered sample of 0.05 g was dispersed in an aqueous solution with a concentration of 1.0×10⁻⁴ mol/l in the dark

Table 1. Nomenclatures of Samples Prepared with Different Concentrations of Nitric Acid to Activated Carbon

Preparation method	Nomenclatures
Activated Carbon + Non (HNO ₃) + Titanium n-butoxide (99.99%)	ACT
Activated Carbon + 0.01M HNO ₃ + Titanium n-butoxide (99.99%)	ACT1
Activated Carbon + 0.05M HNO ₃ + Titanium n-butoxide (99.99%)	ACT2
Activated Carbon + 0.10M HNO ₃ + Titanium n-butoxide (99.99%)	ACT3

atmosphere at room temperature. Each concentration was measured as a function of UV irradiation time from the absorbance in the wavelength range of 250–800 nm of MB measured by the UV/VIS spectroscopy.

Photocatalytic effect

In order to reveal the photocatalytic effect of the samples prepared, the decomposition reaction of MB in water was followed. Powdered samples of 0.05 g were dispersed by ultra sound for 3 minutes. For UV irradiation the UV lamp (20 W, 365 nm) was used at a distance of 100 mm from the solution in a dark box. By sampling 3 ml of solution after removal of dispersed powders by centrifugus, the concentration of MB in the solution was determined as a function of irradiation time from the absorbance change at a wavelength of 660 nm.

Results and Discussion

The Surface characterizations

Figure 1 shows the adsorption isotherms of N₂ at 77 K onto the carbon/TiO₂ composite series prepared by surface modification of activated carbon treated with nitric acid. The isotherms presented in this Fig. 1 show that the total sorption uptake decreases with an increasing amount of nitric acid. All of the isotherms were of Type I as classified by IUPAC. The formation of micropores can be clearly confirmed by the shape of the isotherms. All of the carbon/TiO₂ composites gave Type I isotherms characterized by a plateau which is nearly horizontal to the p/p₀ axis. This means that all the carbon/TiO₂ composites are microporous. The textural properties of the raw materials and carbon/TiO₂ composites are shown Table 2. It can be seen that both the BET surface area and the total pore volume decrease as the distribution of TiO₂ on the activated carbon surfaces after acid treatments. Oh and co-worker [14, 15] report-

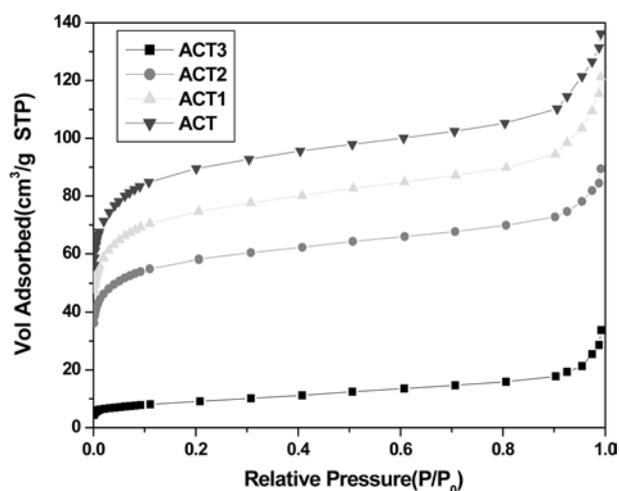


Fig. 1. Adsorption isotherm of N₂ at 77 K onto the carbon/TiO₂ composite series prepared with activated carbon modified by nitric acid.

Table 2. Textural Properties of Pristine Materials and Carbon/TiO₂ Samples Prepared with Different Concentrations of Nitric Acid to Activated Carbon

Sample	Parameter		
	S _{BET} (m ² /g)	Total Pore Volume (cm ³ /g)	Average Pore Diameter (Å)
As-received TiO ₂	132	–	–
Pristine Activated Carbon	1650	0.1201	7.37
ACT	926	0.0851	6.76
ACT1	917	0.0854	5.44
ACT2	854	0.0787	5.41
ACT3	799	0.0704	5.27

ed that the BET surface area is considerably decreased due to the blocking of the narrow pores by surface complexes introduced by the pre-treatment acids. Almost all the surface textural parameters for the composites are a considerably decreased from that of the pristine activated carbon. This can be attributed to the blocking of micropores to titanium complexes by the surface modification of activated carbon when treated with nitric acid. It is expected that the formation of titanium complexes with an increase of the surface functional groups can be blocked from the pores in the activated carbon surfaces, but the porosity of the carbons is reproduced by heat treatment. It is noteworthy that variations of surface parameters among the composite series are related to the removal efficiency of MB by adsorptivity. The pore size distributions (PSD) calculated for carbon/TiO₂ composites using the BJH method are shown in Fig. 2. There is one minor peak 3–4 nm, which is located in the micropore ranges, and another major peak is located ranging from 20 to 50 nm. The pore volume of micropores decreases with an increase in the amount of acid treatment, which is the result of chemical and physical changes by the nitric acid treatment of external surfaces of the carbon/TiO₂ composites.

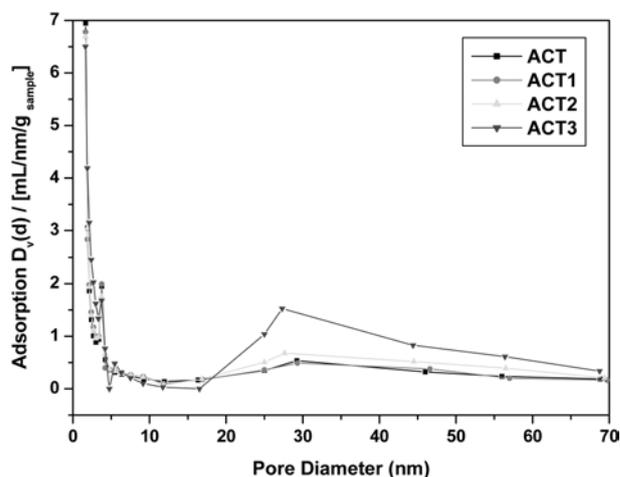


Fig. 2. Pore size distribution, as calculated by the BJH method, of the carbon/TiO₂ composites prepared with TNB.

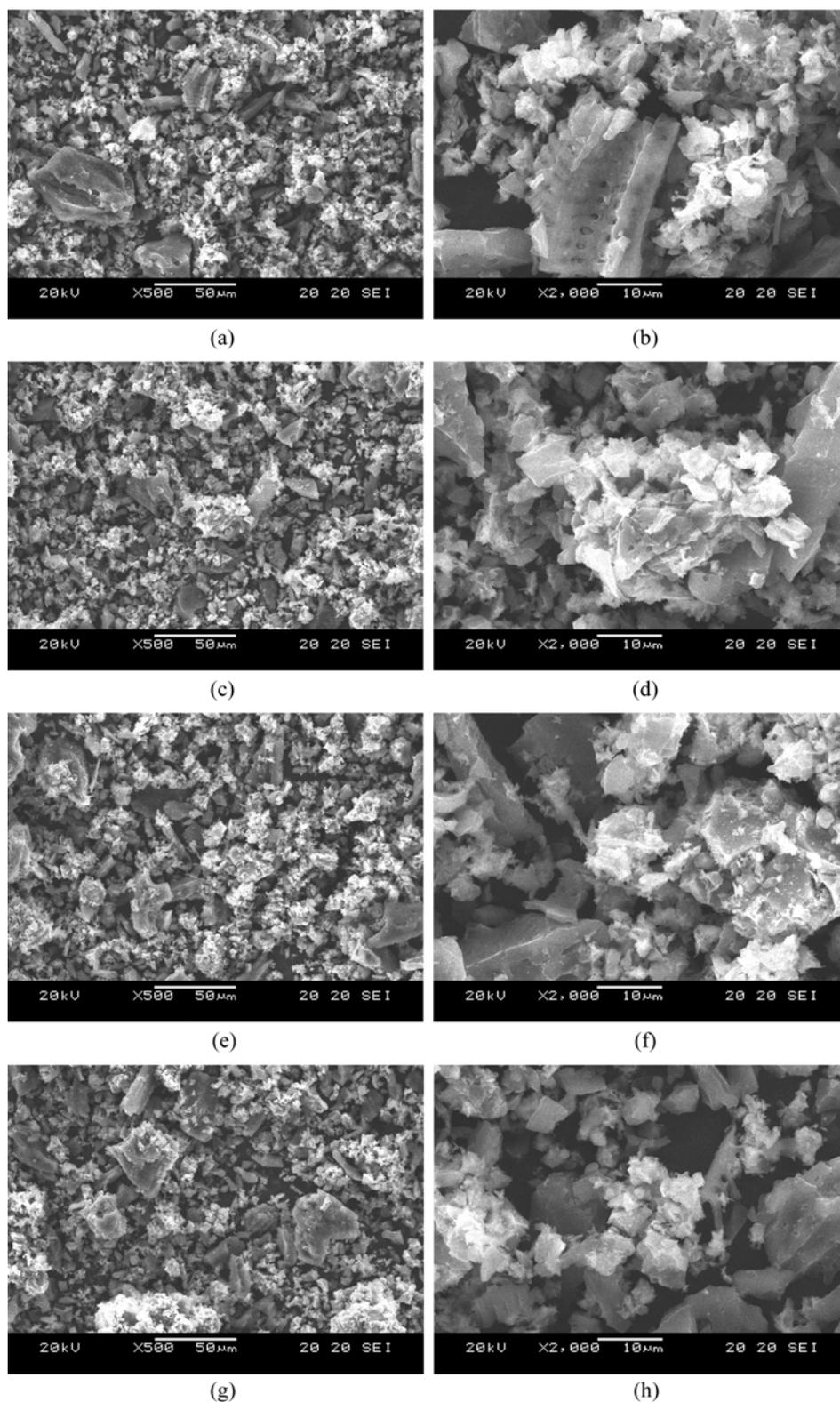


Fig. 3. SEM micrographs of carbon/TiO₂ composites prepared with activated carbon modified by nitric acid; (a) ACT, (b) ACT, (c) ACT1, (d) ACT1, (e) ACT2, (f) ACT2, (g) ACT3 and (h) ACT3.

Figure 3 depicts SEM micrographs of carbon/TiO₂ composite samples. It was observed that titanium complexes were covered with composite particles. The titanium complex particles were regularly distributed on the

carbon, and some large clusters were found when the amount of acid treatment was increased. By contrast, homogenous activated carbon and titanium complexes with good particle dispersions were observed when the

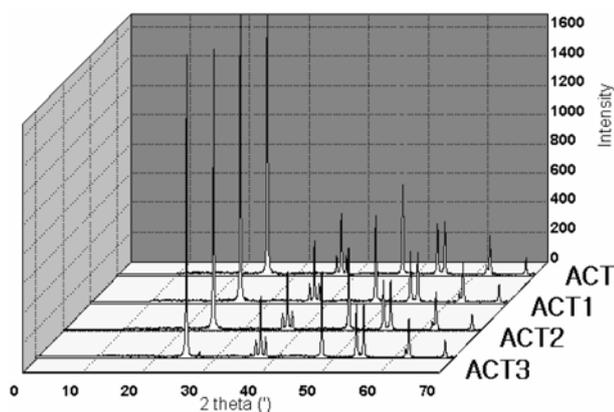


Fig. 4. XRD patterns of carbon/TiO₂ composites prepared with activated carbon modified by nitric acid.

mole concentration of the treatment acid was 0.1 named ACT2. It is considered that a good dispersion of small particles could provide more reactive sites for the reactants than aggregated particles. It has been reported [16] that the photocatalyst of carbon-titanium composite are represented to the quantum efficiency of the electron from the photocatalyst particle interior to the surface and the recombination rate of electron-hole pairs. Accordingly, a high photocatalytic yield is expected for a homogenous and small TiO₂ particle distribution (ACT2 and ACT3). Therefore, the higher photocatalytic activity of the sample ACT2 might be attributed to the homogenous distribution of titanium complexes including titanium dioxide and the adsorptivity of activated carbon. The titanium complexes particles on the carbon surfaces become more pronounced and coarsen by the acid treatment and the size of the particles is increases with an increasing amount of acid.

Structural and chemical identifications

In Fig. 4, changes in XRD patterns are shown on carbon/TiO₂ composites prepared with activated carbon modified by nitric acid. The TiO₂ structure shown is the typical anatase type. After the heat treatment at 973 K for 1 h, the main crystalline phase has not transformed to rutile structure. The major peaks at 25.3, 37.8, 48.0, 53.8, 54.9 and 62.5 are diffractions from (101), (004), (200), (105), (211) and (204) planes of anatase, indicating the TiO₂ prepared existed in anatase state. It can be concluded that the carbon/TiO₂ composites developed have a pure structure of anatase for the all samples.

For the elemental microanalysis of the carbon/TiO₂ composite samples as a function of the amount of acid treatment, these samples were analyzed by EDX. The EDX spectra of the carbon/TiO₂ composites are shown in Fig. 5. These spectra show the presence of C, O and S with strong Ti peaks. The results of EDX elemental microanalysis of the carbon/TiO₂ composite series are listed in Table 3. In the case of most of the samples, carbon and Ti were present as major elements. Also the spectra corresponding to almost all samples show a

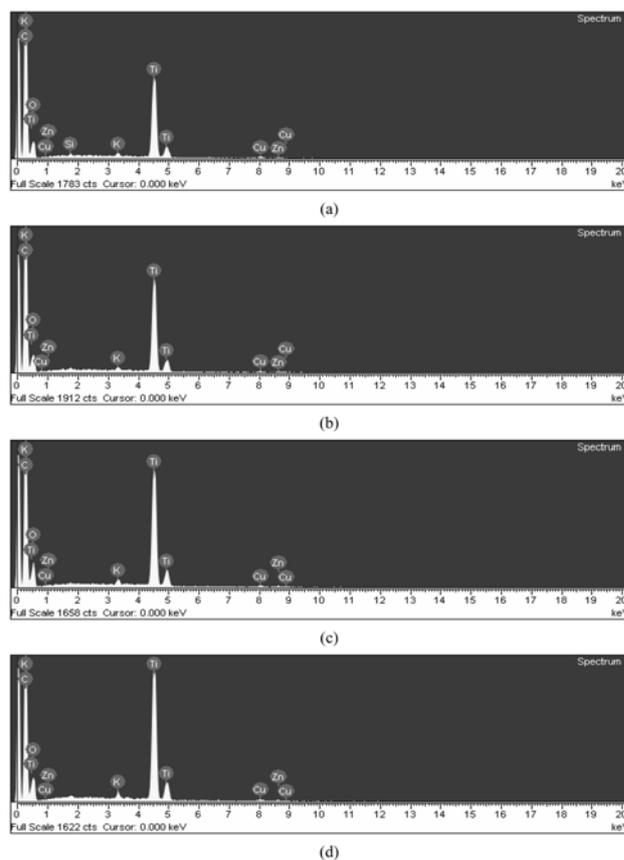


Fig. 5. EDX elemental microanalysis of carbon/TiO₂ composites prepared with activated carbon modified by nitric acid; (a) ACT, (b) ACT1, (c) ACT2 and (d) ACT3.

decrease in C and an increase in O and Ti with an increase in the amount of acid treatment. It should be noted that a decrease of the C and S (impurity elements derived from the pitch) content with an increase of the Ti content is observed for all the sample series.

The FT-IR spectra of the carbon/TiO₂ composite series prepared by surface modification of activated carbon treated with nitric acid are shown in Fig. 6. Observation of the absorption bands shows that the changes between the oxidized (acid treatment) and non-oxidized (non treatment) carbon/TiO₂ composite samples are mainly due to the formation of functional groups. As shown in Fig. 6, the transmittances of the spectra decrease with an increase in the amount of nitric acid treatment. The ν (C-O) mode of the methoxy groups depends on the chemical structure of the adsorption sites. Absorption

Table 3. EDX Elemental Microanalysis (Weight %) of Carbon/TiO₂ Samples Prepared with Different Concentrations of Nitric Acid to Activated Carbon

Sample	C (%)	O (%)	Ti (%)	Cu (%)	Others (%)
ACT	57.8	21.1	18.5	1.17	1.37
ACT1	56.6	21.2	20.3	0.83	1.19
ACT2	51.5	23.2	23.3	0.77	1.24
ACT3	49.5	23.6	24.5	1.03	1.37

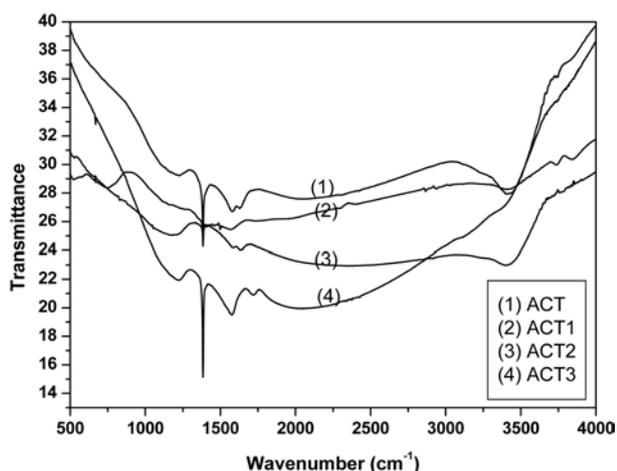


Fig. 6. FT-IR spectra for the carbon/TiO₂ composites prepared with activated carbon modified by nitric acid.

of C-O followed by measurement of IR spectra has been used to characterize treated and non-treated metal catalysts [17]. The frequency of ν (C-O) of adsorbed carbon monoxide is often treated as an indicator characterizing the local coordination. This is also suitable for examining the state of metal ions situated differently on the solid surface. The most characteristic changes are observed at 1380 and 1719 cm⁻¹ in the presence of C-O- and N-O- containing structures. The band centered at 1719 cm⁻¹ is ascribed to the stretching vibrations of carboxyl groups on the edges of layer planes or to conjugated carbonyl groups. The weak band appearing at 1380 cm⁻¹ is ascribed to the formation of

oxygen functional groups such as a highly conjugated C=O stretching in carboxylic groups, and carboxylate moieties [18]. These results indicate that the acid treatment gave rise to a greater increase in C=O bonds in carboxylic acid and lactone groups. The acid treatment is consequently associated with an homogeneous distribution of titanium and formation of titanium complexes with the increased surface acidity of the activated carbons. Another significant conclusion from Fig. 6 is that the concentrations of C-H bonds are outstanding, as the C-H absorption bands in the 1400-1300 cm⁻¹ (bending modes) regions are absent from the spectra. Since C-H bonds are abundant in a carbon/TiO₂ composite, it seems that the precursor species dissociate on the substrate leaving O, Ti and possibly C, while all the byproducts containing C-H bonds are chemisorbed. Despite differences in the amount of acid treatment of the various samples, all the spectra exhibit a strong absorption band due to O-H stretching vibrations, indicating the presence of oxygen functional groups in the carbon/TiO₂ composite series. A broad band in the 3100-3500 cm⁻¹ region, typically attributed to O-H stretching from hydroxyl, phenolic and carboxylic groups is absent. Thus FT-IR spectra confirm the formation of carbonyl groups during the oxidation process by the acid treatment. The main goal of the oxidation is to obtain a more hydrophilic surface with a relatively large number of oxygen-containing oxygen groups on the carbon surfaces. If the O-H stretching absorption is totally, or in part, due to the acid treatment, then another absorption band, corresponding to the O-H bending

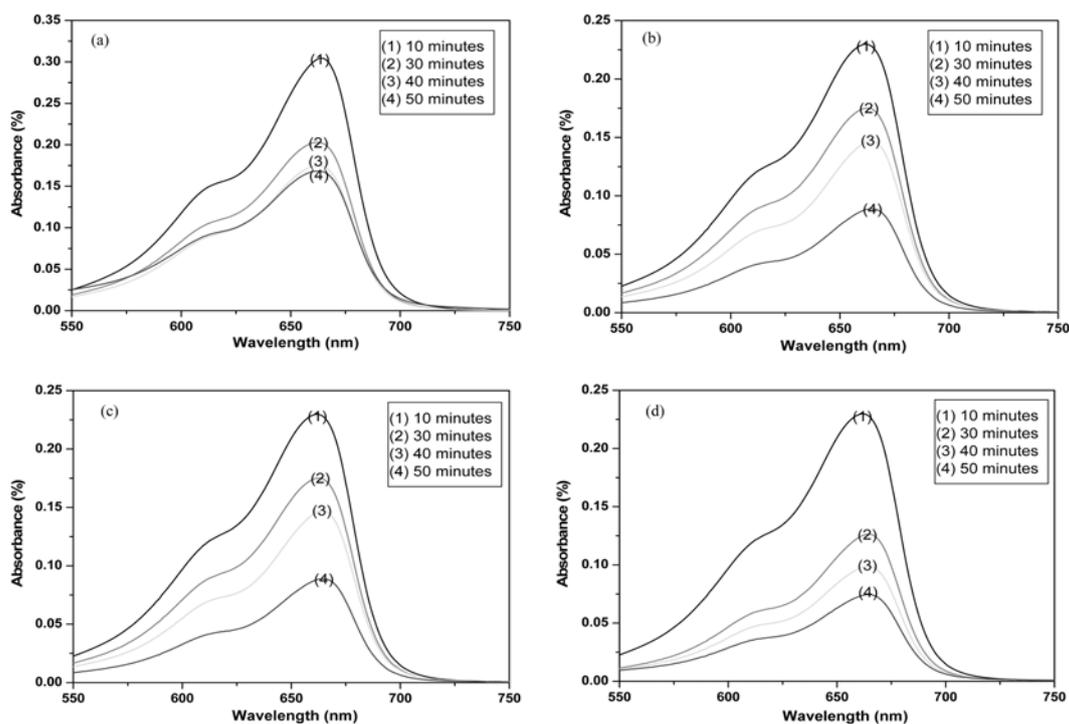


Fig. 7. UV/VIS spectra of MB concentration against the carbon/TiO₂ composite under various time conditions; (a) ACT, (b) ACT1, (c) ACT2 and (d) ACT3.

vibration, is expected in the spectra. In the acid treatment, this band has a frequency of 1595 cm^{-1} [19] but for chemisorbed O-containing functional groups by the acid treatment it must change as the bending mode would be strongly hindered by surface forces. It is thus possible that the O-H bending frequency is shifted to lower frequencies. The low absorption intensity due to the Ti-O bonds in most spectra of Fig. 6 may be related to the amorphous nature of the carbon/TiO₂ composite series and to further distortions on their structure due to the incorporation of carbon and excess oxygen.

Photocatalytic activity

The UV/VIS absorbance spectra of MB concentration at $1.0 \times 10^{-4}\text{ mol/l}$ against the carbon/TiO₂ composite series prepared by surface modification of activated carbon treated with nitric acid are shown in Fig. 7. As can be seen from the spectra, the absorbance maxima for the all samples slowly decrease with an increase of UV irradiation time. This indicates that the transparency of the MB concentration increases greatly by the photocatalytic degradation effect of carbon/TiO₂ composites. Figure 8 shows changes in MB concentration under UV light irradiation in the solution. MB removal with carbon/TiO₂ composite photocatalysts is carried out to observe the UV photolysis effect for the MB solution. It is observed that the MB solution is quite unstable with a variation of concentration when it is irradiated under UV with carbon/TiO₂ composites, suggesting the disappearance of MB is caused by UV irradiation. The changes are plotted on the relative concentration (c/c_0) of MB in the aqueous solution with UV irradiation time for the carbon/TiO₂ composite series. The relationship shows approximately linear properties depending on irradiation time, as reported on similar modified TiO₂ samples [20, 21]. Because the presence of activated carbon in carbon/TiO₂ composite has a large adsorptivity, as mentioned above, it is believed that the decrease of MB concentration in the aqueous solution can

occurred by two physical phenomena such as adsorption by the activated carbon and photo-degradation by the TiO₂ formed on the carbon surfaces. In a former study [22], MB adsorbed on the carbon particles can be eventually decomposed by the TiO₂ particles in the solution. This suggests that the TiO₂ formed on the surface of activated carbon can retain its photocatalytic reactivity. The synergistic effect has been ascribed [22] to the enhanced adsorption of the pollutants on activated carbon followed by a transfer through an interphase to titania. In this study, the excellent photocatalytic activity of the carbon/TiO₂ could be attributed to the homogeneous distribution of titania complexes on the external surfaces and excellent adsorptivity of activated carbon. The surface oxidation of activated carbon by acid treatment could occur by the acid-base character of the surface active sites of the oxides. The acid-base character of the surface active sites of the oxides can be determined by means of indirect determinations, such as measurements of the catalytic activity for the decomposition of pollutants [8]. From the removal results of MB in the solution measured periodically over 60 minutes an increase in the amount of nitric acid results in a significant degradation effect with a decrease of the relative concentration (c/c_0) of MB. The TiO₂ deep inside the activated carbon is not easily accessible to light because of enhanced reflection and scattering by the support and the long distance to travel. For all the carbon/TiO₂ composites prepared by surface modification of activated carbon treated with nitric acid, the slope relationships between c/c_0 of MB and UV irradiation time were observed to be $1.0 \times 10^{-4}\text{ mol/l}$ of MB concentration. From the results between c/c_0 of MB and UV irradiation time, it was observed that the removal efficiency of MB for the composites was much better than that of pristine TiO₂. Based on these observations, we therefore can conclude that the decrease of MB concentration should be attributed to both the effects between photo-degradation of the supported TiO₂ and adsorptivity of the activated carbon.

Conclusions

In this study, we have prepared carbon/TiO₂ composite photocatalysts through surface modification of activated carbon treated with nitric acid. The prepared composite materials were characterized in terms of surface properties, structural crystallinity between activated carbon and TiO₂, elemental identification, surface functional groups and photocatalytic activity. The conversion of TNB to TiO₂ during the heat treatment must be important for the preparation of carbon/TiO₂ composites. From the surface textural properties, both the BET surface area and the total pore volume decreases as does the distribution of TiO₂ on the activated carbon surfaces after acid treatments. According to the SEM micrographs, the titanium complex particles are regularly

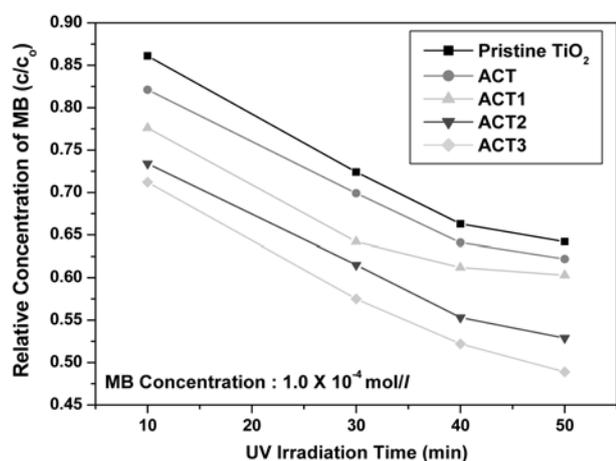


Fig. 8. Dependence of relative concentration (c/c_0) of MB in the aqueous solution on time of UV irradiation for the carbon/TiO₂ composites prepared with activated carbon modified by nitric acid.

distributed on the carbon, and some large clusters were found when the amount of acid treatment was increased. The changes in XRD patterns are shown to be typical of anatase type on carbon/TiO₂ composites prepared with activated carbon modified by nitric acid. The EDX results of carbon/TiO₂ composites show the presence of C, O and S with strong Ti peaks. Observation of the absorption bands for the FT-IR spectra show that the changes for the carbon/TiO₂ composites prepared with activated carbon modified by nitric acid are mainly due to the formation of functional groups. Finally, the prominent photocatalytic activity of the carbon/TiO₂ composites between c/c_0 of MB and UV irradiation time could be attributed to both the effects between photocatalysis of the formation of titania complexes and adsorptivity of the activated carbon.

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